RESEARCH NOTE

Stability of the AB crystal for asymmetric binary hard sphere mixtures

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The thermodynamic stability of the AB (rocksalt) structure for binary mixtures of hard spheres is established by means of Monte Carlo and molecular dynamics simulations. Constant pressure and constant volume phase diagrams are presented for size ratios $\sqrt{2} - 1$ and 0.45. A phase-separation molecular dynamics experiment is described, confirming the predictions of the phase diagram.

The finding that binary mixtures of hard spheres may crystallize spontaneously into ordered superlattices has provoked considerable interest. Crystals of stoichiometry AB_{13} and AB_2 (where A is the large particle) were observed in colloidal suspensions of particles with steeply repulsive potentials by Bartlett *et al.* [1] and the thermodynamic stability of these structures for true hard spheres was confirmed in computer simulations by Eldridge and co-workers [2, 3] This appears to present a paradox [4] as the formation of these ordered structures is caused by the entropy, normally associated with the driving force for disorder, since the potential energy in hard-particle systems is zero. Understanding the factors which control crystal structures in colloids has become a matter of technical importance, since colloidal crystals may exhibit potentially useful optical [5] and acoustic properties. More generally, it has been suggested that the same packing considerations which dictate the ordered structures of hard particles may govern the stoichiometry of the compounds which form in van der Waals mixtures (e.g., CH_4/H_2) at very high pressures [6] though other workers have maintained the importance of energetic factors [7] in these systems. Certainly, the hard sphere model is an important reference system for perturbation theories of mixtures, which can be applied to alloys or van der Waals crystals [8]

The entropy 'paradox' is resolved by noting that in an ordered system at high density a particle may explore a larger volume about its lattice site than is available in a disordered system at the same density, and that the consequential gain in translational entropy may compensate for the loss of entropy associated with the formation of

the ordered structure [4] Murray and Sanders [9] formulated the principle that an ordered compound would form only if its packing fraction ϕ (the fraction of space contained in the interior of the particles) when close packed exceeded that of the one-component crystals into which it would separate ($\phi_{cp}^{(1)} = \pi\sqrt{2}/6 \simeq 0.7405$ for fcc or hcp structures). For a lower packing fraction the particles in such a compound will have a larger free volume in which to move, and thus a higher entropy. This principle accounts for the stability of the AB_2 system, for a particle radius ratio α, $0.48 < \alpha < 0.62$, which is (roughly) where it is observed. It also predicts a window of stability for an AB compound, of the NaCl structure, for $\alpha \sim 0.414 \simeq \sqrt{2} - 1$, for which $\phi_{cp}(\alpha = \sqrt{2} - 1) = 0.793$ comfortably exceeds that of monodisperse hard spheres. The principle does not, however, predict the observed stability of the AB_{13}, system for which the maximum packing fraction $\phi_{cp}(\alpha = 0.558) = 0.738$. Recently, Cottin and Monson [10] have developed a cell theory of binary hard particle crystals, which contains a more precise estimate of the free volume. Their results for the free energies of the AB_2 and AB_{13} crystals and for the binary phase diagrams involving them are in remarkably good agreement with those obtained in the computer simulations.

The purpose of the present work is to report on the thermodynamic stability of the AB (rocksalt) phase on the basis of the same free-energy calculations used previously [2] (we have already reported that AB (CsCl) is unstable [3]). This phase has not been detected experimentally in colloidal suspensions. The appearance of the AB phase, expected on packing arguments for a relatively small size ratio ($\alpha < 0.45$), would set a lower
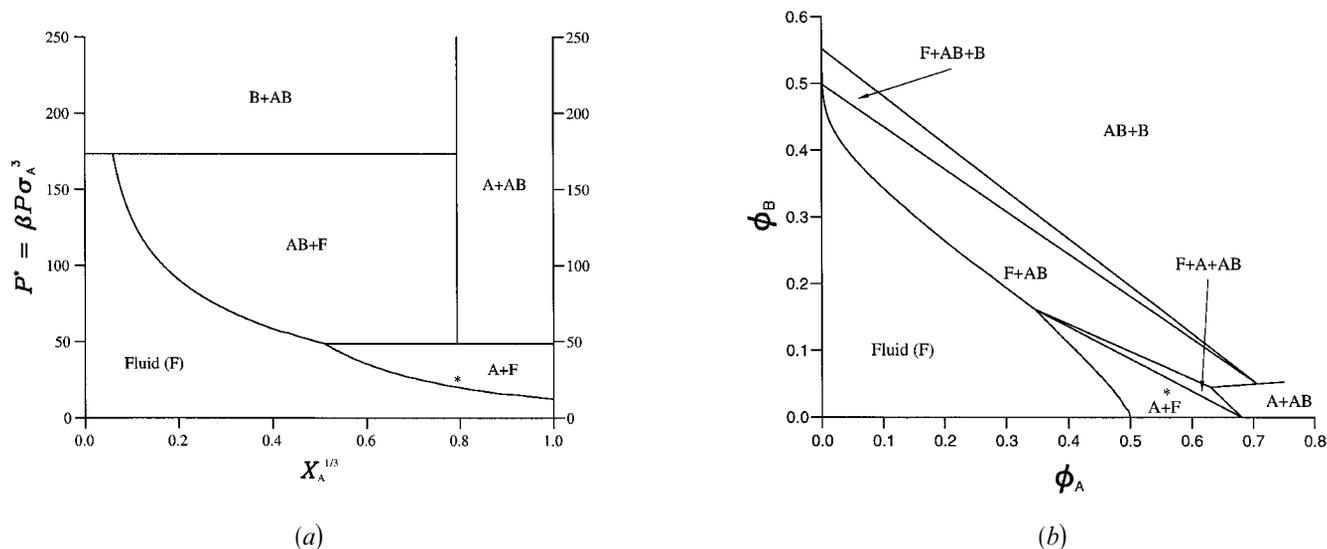
Figure 1. (a) P–X phase diagram of a binary mixture of hard spheres with a diameter ratio $\alpha = 0.414$. (b) Constant volume diagram: the lines indicate boundaries of two or three phase regions. Note that the ordinate in (a) is $x_A^{1/3}$. The star marks the phase point used as the starting point of the MD run.
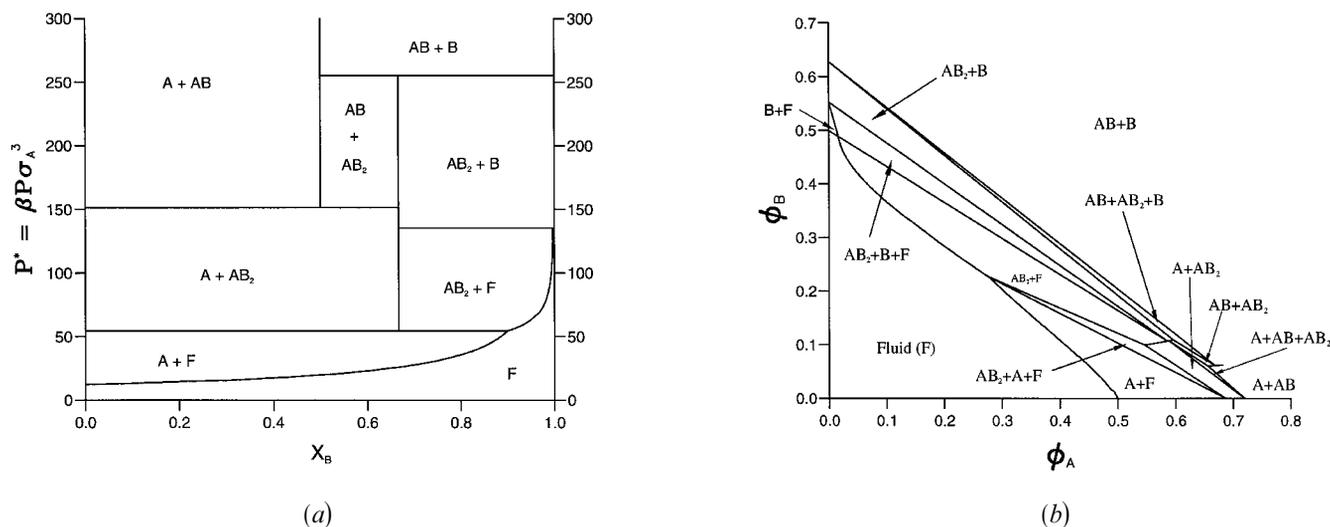

Figure 2. Constant P and V phase diagrams for $\alpha = 0.45$.

bound in α to the range of observability of the more exotic AB_2 crystal. It was not included in the phase diagrams reported previously [3] but it has already been considered in cell theory calculations [10]

Results are reported at $\alpha = 0.414$, where AB should be most stable (since the small particles will just fill the octahedral holes in the fcc lattice of large particles) and at $\alpha = 0.45$ which might be expected to be close to its upper limit of stability. The competing phases considered are the binary fluid (expected at low packing fractions), pure fcc crystal (A and B), and AB_2. The data concerning the AB_2 superlattice were taken from [2] for the diameter ratios considered ($\alpha \leqslant 0.45$) AB_{13} cannot

be found (cf. [2]). The Gibbs free energies of all phases were determined by thermodynamic integration [11] For the binary fluid, the semi-empirical equation of state of Mansoori *et al.* [12] was used, allowing the free energy to be known analytically. For the solid state, the method of Frenkel and Ladd [13] was implemented, taking the reference state, of known free energy, as the corresponding Einstein crystal, which can be reached by slowly turning on harmonic springs to bind the particles to their lattice sites. The method is discussed in detail in [2] and requires Monte Carlo calculations. The results were checked by direct integration of the equation of state between selected state points.
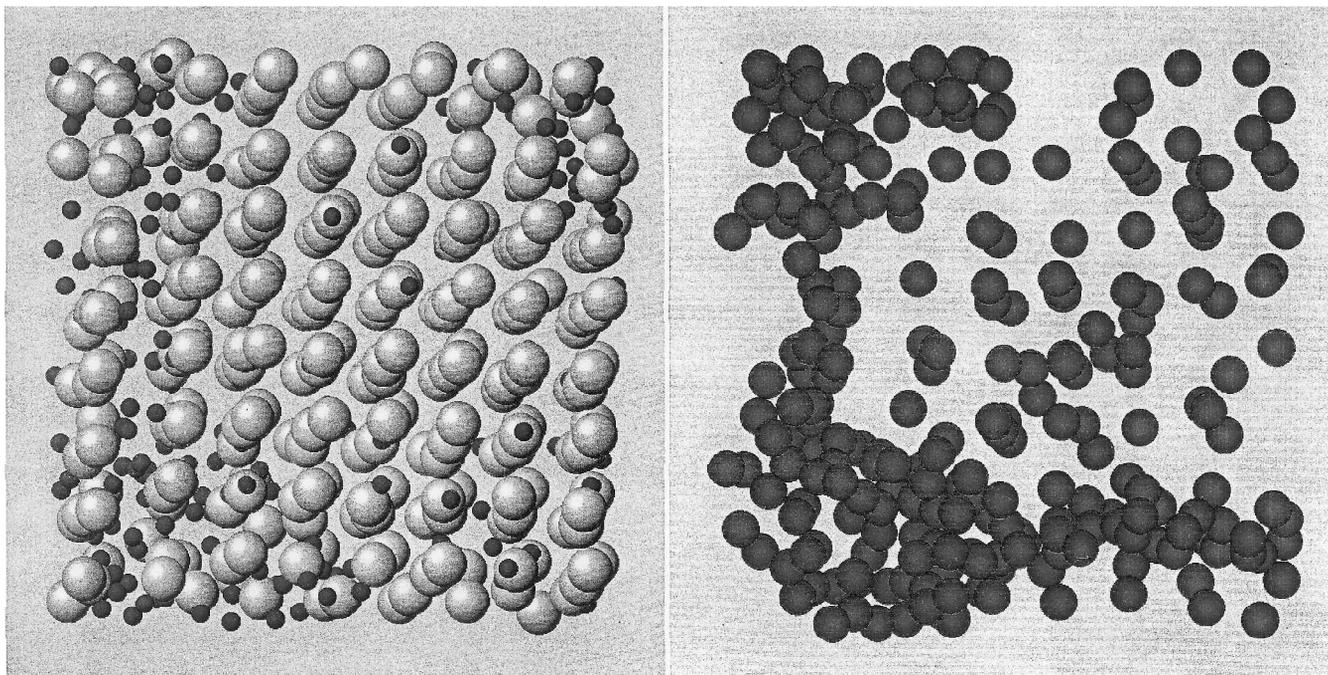
Figure 3.   The left hand panel shows the arrangement of large (yellow) and small (red) spheres in the last configuration of the molecular dynamics simulation. For convenience, the radii of each species have been drawn half their actual value. The right hand panel shows the small spheres full-size and the large spheres are omitted.

We present the pressure–composition phase diagrams, derived from the classical double-tangent construction (see [3]), for diameter ratios $\alpha = 0.414$ in figure 1(a) and $\alpha = 0.45$ in figure 2(a). As anticipated, at $\alpha = 0.414$ AB is the dominant compound observed in the solid part of the phase diagram, and AB_2 is no longer observed at such small diameter ratios. Note that a pure A solid would crystallize out of an equimolar fluid mixture $(x_A = x_B = 1/2)$, rather than AB, in agreement with Denton and Ashcroft's theoretical finding that the AB crystal was unstable in such a mixture [14] For $\alpha = 0.45$, the AB structure coexists with the AB_2 superlattice, but is observable only at very high pressures, showing that it is very close to its upper stability limit. For intermediate pressures, there is a tendency for fcc solid A (large spheres) to precipitate, but the AB + fcc B + fluid eutectic corresponds to a composition $x_B \simeq 1$ so that the B + fluid coexistence is confined to a very tiny region. Overall, the calculated phase diagrams are in good agreement with the cell model theoretical results [10] although the predicted stability limits of each phase differ somewhat.

Pressure–composition phase diagrams are not very relevant when it comes to comparing the data with experiments on colloidal suspensions [1] The total volume accessible to a colloidal mixture is set by the suspending fluid. Hence, constant volume phase diagrams have been computed [3] using the partial packing fractions as independent coordinates. in such a diagram, the lines passing through the origin correspond to a constant composition and the lines parallel to the second bisectrix are of equal total packing fraction. Figures 1(b) and 2(b) show the representations obtained for $\alpha = 0.414$ and $\alpha = 0.45$. Figure 1(b) shows that AB crystals should be readily preparable in colloidal suspensions of this size ratio, but a large excess of the smaller B particles is required in the mixture.

As a final step we examine by means of molecular dynamics simulations whether the system can reach the predicted equilibrium state. The calculation provides a check on the accuracy of the thermodynamically deduced phase diagram and also gives some insight into the phase kinetics of the hard-particle system. We consider an MD simulation started from an AB crystal with $\alpha = \sqrt{2} - 1$ and with a packing fraction of 0.6. As figure 1 shows (the relevant composition is shown by the stars in the figures) the AB crystal is metastable under these conditions (at $P^* = 28$ in figure 1(a)); the thermodynamic equilibrium state should be coexistence of fcc A + fluid with $x_{fluid}B = 0.7$. Applying the lever rule to figure 1(a) gives the following equilibrium composition for the system; 71.7% fluid and 28.3% fcc A. Thus, 56.6% of the large spheres should stay on lattice sites and the remainder should be found in a fluid state with all the small ones. The evolution of the system can be followed by saving periodically the diffusion constants

of large and small spheres, and a 'melting factor' $\mathscr{M}$ defined as the average of (200), (020) and (002) structure factors of the crystal $\left(N^{-1}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\{i\mathbf{k}\cdot\mathbf{r}^{ij}\}\right)$ where N is the total number of atoms, 512). For the perfect AB structure, $\mathscr{M} = N$, whereas in the liquid state, $\mathscr{M} \simeq 1$. Consistently with the predictions of the phase diagram, the melting factor after 10^5 collisions per particle has converged to a result remarkably close to the theoretical value $\mathscr{M} \sim (0.283)^2 N$ and the diffusion constants for the small spheres have reached a constant value. Finally, a useful probe is the direct visualization of the final configuration of the molecular dynamics simulations. Figure 3 shows the last configuration of the 30 million collision run. A central, crystalline region of large spheres depleted in small ones is seen to coexist with a fluid of large and small spheres. For the central domain, the former fcc structure remains with an A—A separation very similar to that in the parent AB crystal, indicating that phase separation has occurred in accordance with the predictions of the phase diagram. Given the relatively weak thermodynamic driving forces which one imagines to be associated with the entropy, it seems remarkable that this mesocopic reorganization is observed on this timescale.

Overall, these results provide further confirmation of the reliability of the predictions emerging from cell model theory [10], which are achieved with far less effort. Some quantitative differences are seen in the phase diagrams but, given the sensitivity of these diagrams to the thermodynamic properties of the pure phases, this is unsurprising. Cottin and Monson [10] have surveyed the possible compounds which might be found in hard sphere mixtures and concluded that AB_{13}, AB_2 and AB (rocksalt) are the only ones likely to form.

This observation would seem to suggest that energetic factors play a role in the formation of van der Waals compounds [6, 7] since other stoichiometries have, so far, been observed.

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